Inorg. Chem. **1998,** *37,* 5651−5656

Construction of Copper(I) Coordination Polymers of 1,2,4,5-Tetracyanobenzene with Zigzag Sheet and Porous Frameworks

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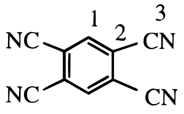
Received April 16, 1998

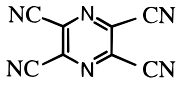
This paper describes two copper(I) supramolecules with the same anion and cation but quite different topologies and properties. The reaction of $[Cu(CH_3CN)_4]PF_6$ and 1,2,4,5-tetracyanobenzene (TCNB) leads to two novel polymeric coordination compounds, $[Cu_2(TCNB)_3](PF_6)_2(Me_2CO)_4$ **(1)** and $[Cu_2(TCNB)_3](PF_6)_2$ **(2)**, depending on the solvents used. The crystal structures have been determined by single-crystal X-ray diffraction. Crystal data are as follows. **1**: $C_{21}H_{15}N_6O_2CuPF_6$, monoclinic, $P2_1/a$, $a = 11.553(4)$ Å, $b = 16.135(7)$ Å, $c = 15.046(3)$ Å, $\beta = 108.08(2)°$, $Z = 4$. **2**: $C_{15}H_3N_6CuPF_6$, orthorhombic, *Cmcm*, $a = 28.282(3)$ Å, $b = 10.337(3)$ Å, $c = 16.285(4)$ Å, $Z = 16$. In both polymers, copper(I) ions have similar pseudotetrahedral environments and the four coordination sites are fully occupied by the four bridging ligands, two μ_2-TCNB and two μ_4-TCNB groups. Polymer **1**, obtained in acetone, revealed a two-dimensional zigzag sheet network between copper(I) ions, whereas **2**, synthesized in methylethyl ketone, displayed a three-dimensional porous framework with different functional groups (or atom) in different cavities. The redox, magnetic, and conductive behaviors of both complexes are discussed. It is demonstrated that the two complexes give different physicochemical properties.

Introduction

The recent efforts in crystal engineering of networked materials based on polymeric coordination compounds have been devoted to the use of multifunctional ligands.[1−3] The ligand 1,2,4,5-tetracyanobenzene (TCNB) and its analogues such as tetracyanoethene (TCNE), 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), and 2,3,5,6-tetracyanopyrazine (TCNP) have recently attracted much interest because of their variable coordination behavior,[4−6] tendency to form polymers with infinite networks,[7] and facile reduction to radical anions or dianions[5,6,8] as well as their interesting electronic and magnetic behaviors.[6−9] In this ligand family, the complexes of Ru−TCNX (TCNX = TCNE, TCNQ, TCNP, and TCNB),[8] Os−TCNX (TCNX = TCNB, TCNQ), M−TCNE (M = Rh, Mn, Cr, W, Fe, Cu, Co),[7,9−11] and M−TCNQ (M = Mo, Ag, Mn, Cr, W)[11−13] have been reported. These studies, however, mainly focused on the electronic transfer and magnetic properties of the complexes. Only a few concerned the structural characterization.[7,10,12,14]



TCNB



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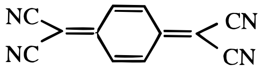
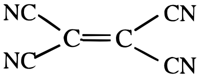


TCNQ



TCNE

The rapidly growing interest in self-assembled infinite metal complexes with specific network topologies, owing to their potential as new functional solid materials,[15,16] has directed much attention toward the structural building, deliberate design, and control of polymeric coordination compounds.[7,12,17] Generally, the network topology can be controlled and modified by selecting the chemical structure of ligands,[2,17] which can lead

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10.1021/ic980427v CCC: $15.00

to special intermolecular interactions, coordination geometry of metals, inorganic anions,[2] and sometimes the ratio of metal salt to ligand.[3] By contrast, though a number of studies about effects of solvent on the properties of compounds or coordination compounds have been reported,[18−20] considerably less is known about topological control of coordination compounds by solvent and few solvent-responsive structure changes are reported.[21] With an aim to design novel and functional metal complex supermolecules, we have reported a number of copper(I) and silver(I) polymeric complexes with remarkable features by selecting the intermolecular interactions such as hydrogen-bonding,[22,23] $\pi-\pi$ stacking,[24−26] S···S contacts,[27] and coordination bonds.[17,25−30] Expectantly, the proper selection of solvent in the synthetic process can bring about another approach to the control of self-assembly of coordination compounds. Here, we present two unique copper(I) coordination polymers of TCNB having the same anion and cation but different topologies and properties, depending on whether the solvent is acetone or methylethyl ketone.

Experimental Section

General Methods. Preparations were carried out under an argon atmosphere using usual Schlenk techniques. All solvents were dried and distilled by standard methods before use. TCNB was purchased from Wako Chemical Co., Japan, and used without further purification. $[Cu(CH_3CN)_4]PF_6$ was synthesized and purified according to literature procedure.[31] IR spectra were measured on a JASCO FT/IR-8000 spectrometer using KBr disks. ESR spectra were obtained on a JEOL JES-TE200 ESR spectrometer. NMR spectra were recorded using a JEOL GX-270 NMR spectrometer. Electronic conductivity was determined by a conventional two-probe technique at room temperature with compacted pellets. Cyclic voltammetric measurements were carried out using a polarographic analyzer P-1100 (made in Japan) with Ag/AgCl reference and Pt working and counter electrodes.

Synthesis of $[Cu_2(TCNB)_3](PF_6)_2(Me_2CO)_4$ (1). Solid TCNB (89.5 mg, 0.50 mmol) was added to a stirred solution of $[Cu(CH_3CN)_4]PF_6$ (37.2 mg, 0.1 mmol) in 10 mL of acetone at room temperature. The yellow solution, which formed immediately, was transferred to a 6 mm diameter glass tube and layered with *n*-pentane. The glass tube, sealed under Ar, was left standing at room temperature for 1 week; yellow brick crystals suitable for single-crystal X-ray analysis, corresponding to **1**, were obtained. The crystals are unstable. They will lose their clarity and decompose upon drying, probably due to the loss of the acetone molecule incorporated in the crystals. IR (KBr, cm^{-1}): 2245 ($\nu_{C\equiv N}$), 841 ($\nu_{PF_6^-}$). ^1H NMR [23 °C, $(CD_3)_2CO$, 270 MHz]: for **1**, δ 8.94 (2H, Ar−H); for TCNB, δ 8.90 (2H, Ar−H). ^{13}C NMR [23 °C, $(CD_3)_2CO$, 68 MHz]: for **1**, δ 139.3 (C_1), 121.3 (C_2), 114.2 (C_3); for TCNB, δ 139.2 (C_1), 121.2 (C_2), 114.4 (C_3). Anal. Calcd for $C_{15}H_3N_6CuPF_6$ (without including acetone): C, 37.8; H, 0.6; N, 17.7%. Found: C, 38.8; H, 0.6; N, 17.1% (a slight difference between calculated and observed values may be due to the loss of the acetone).

Table 1. Crystal Data for $[Cu_2(TCNB)_3](PF_6)_2(Me_2CO)_4$ **(1)** and $[Cu_2\ (TCNB)_3](PF_6)_2$ **(2)**

	1	**2**
formula	$C_{21}H_{15}N_6O_2CuPF_6$	$C_{15}H_3N_6CuPF_6$
m fw	591.90	237.87
space group	$P2_1/a$	*Cmcm*
cryst syst	monoclinic	orthorhombic
T, K	296	296
a, Å	11.553(4)	28.282(3)
b, Å	16.135(7)	10.337(3)
c, Å	15.046(3)	16.285(4)
β, deg	108.08(2)	
V, Å^3	2666(1)	4760(3)
Z	4	16
ρ_{calcd}, g cm^{-3}	1.475	1.327
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
μ, (Mo Kα), cm^{-1}	9.50	10.40
R,[a] R_w[b]	0.069, 0.080	0.057, 0.063

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Synthesis of $[Cu_2\ (TCNB)_3](PF_6)_2$ (2). Similar to the synthesis of **1**, solid TCNB (89.0 mg, 0.5 mmol) was added to a solution of $[Cu(CH_3CN)_4]PF_6$ (37.2 mg, 0.1 mmol) in 10 mL methylethyl ketone at room temperature and stirred for a while. The resulting yellow suspension was filtered, and the filtrate was transferred to a 6 mm diameter glass tube. To obtain a fine quality single crystal, this saturated solution does not need any diffusion solvent. The glass tube was sealed under Ar and kept at room temperature for 1 week; yellow brick crystals similar to **1** in shape were isolated, corresponding to **2**. IR (KBr, cm^{-1}): 2245 ($\nu_{C\equiv N}$), 843 ($\nu_{PF_6^-}$). NMR spectra are the same as those of **1**. Anal. Calcd for $C_{15}H_3N_6CuPF_6$: C, 37.8; H, 0.6; N, 17.7%. Found: C, 37.9; H, 0.6; N, 17.0%.

X-ray Crystallography. Crystal data for **1** and **2** are given in Table 1. The crystal suitable for X-ray measurements was fixed on a glass fiber with adhesives. For **1**, the crystal was coated with paraffin to avoid the loss of its clarity. Diffraction data for **1** and **2** were collected at room temperature on Rigaku AFC5R and Rigaku AFC7R four-circle diffractometers equipped with graphite-monochromated Mo Kα radiation in the $\omega-2\theta$ scanning mode, respectively. The intensities of three representative reflections, measured after every 150 reflections, remained constant throughout data collection for complex **2**, indicating crystal and electronic stability, so no decay correction was applied. For polymer **1**, the standard decreased by 0.4% over the course of data collection. A linear correction factor was applied to the data to account for this phenomenon. Azimuthal scans of several reflections for each compound indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (MITHRIL for **1**, SAPI91 for **2**),[32] expanded using Fourier techniques, and refined by full-matrix least-squares minimization of $\sum w(|F_o - F_c|)^2$ with anisotropic thermal parameters for all of the non-hydrogen atoms. The positions of all the hydrogen atoms were determined from difference electron density maps and included but not refined. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[33] All of the

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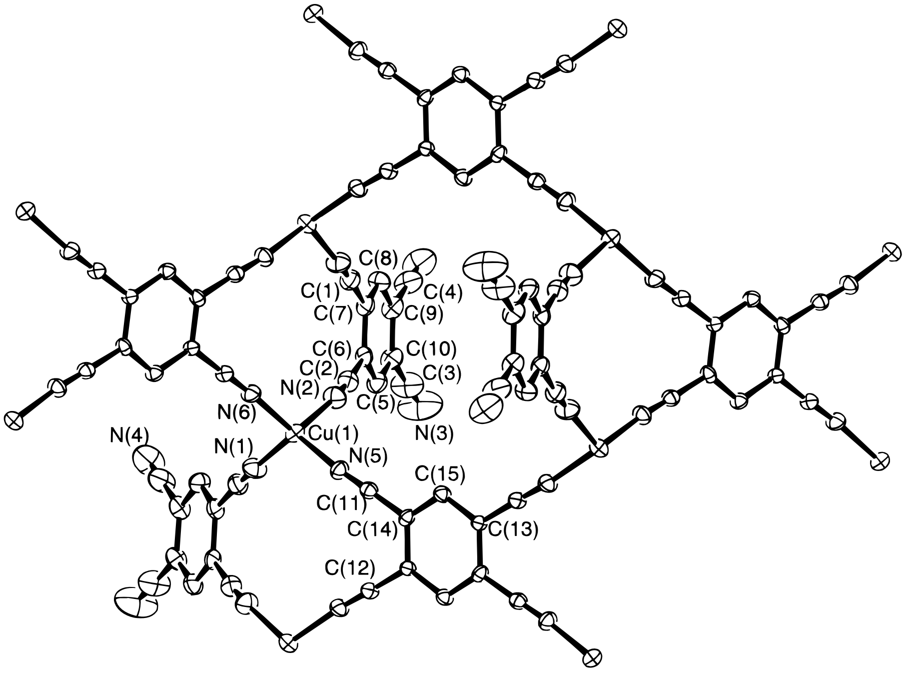

Figure 1. ORTEP drawing with atom-numbering scheme in **1** showing 40% probability level (acetone molecules and PF_6^- were omitted for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Cu_2(TCNB)$_3$](PF_6)$_2$(Me_2CO)$_4$ (**1**) and [Cu_2 (TCNB)$_3$](PF_6)$_2$ (**2**)

	1		
Cu(1)−N(1)	2.009(7)	Cu(1)−N(5)	1.961(7)
Cu(1)−N(2)	1.998(7)	Cu(1)−N(6)	1.951(7)
N(1)−Cu(1)−N(2)	95.0(3)	N(2)−Cu(1)−N(5)	107.7(3)
N(1)−Cu(1)−N(5)	119.4(3)	N(2)−Cu(1)−N(6)	115.8(3)
N(1)−Cu(1)−N(6)	107.5(3)	N(5)−Cu(1)−N(6)	110.9(3)
	2		
Cu(1)−N(1)	1.983(5)	Cu(1)−N(1′)	1.983(5)
Cu(1)−N(2)	1.969(5)	Cu(1)−N(3)	1.943(5)
N(1)−Cu(1)−N(1′)	104.0(3)	N(1)−Cu(1)−N(2)	105.6(2)
N(1)−Cu(1)−N(3)	111.3(2)	N(1′)−Cu(1)−N(2)	105.6(2)
N(1′)−Cu(1)−N(3)	111.3(2)	N(2)−Cu(1)−N(3)	118.0(2)

calculations were performed using the TEXSAN package.[34] The selected bond distances and angles for **1** and **2** are listed in Table 2.

Results and Discussion

Structure of [Cu_2(TCNB)$_3$](PF_6)$_2$(Me_2CO)$_4$ (1). In addition to the results of IR and NMR analyses, indicating the existence of the new compound in the solid state (crystals) and in solution, respectively, X-ray crystal structure determination reveals details about the coordination pattern. Figure 1 shows the ORTEP drawing of local coordination around the copper(I) atom with the atom-numbering scheme. There exist two kinds of coordinated TCNB molecules, namely μ_2-TCNB and μ_4-TCNB, in the polymeric cation [Cu_2(TCNB)$_3$]$^{2+}$. Each copper atom adopts a slightly distorted tetrahedral geometry comprised of four cyano-nitrogen atoms from two μ_2-TCNB and two μ_4-TCNB moieties. The four Cu−N bond lengths are in the range of 1.951(7) −2.009(7) Å, comparable to those found in previously reported cyano- or pyrazine-coordinated copper(I) complexes (1.924−2.030 Å).[16,17,22] It is noted that the Cu−N bond lengths for μ_4-TCNB (1.951(7) and 1.961(7) Å) are significantly shorter than those (1.998(7) and 2.009(7) Å) for μ_2-TCNB, indicating a stronger coordination of copper(I) to the cyano-nitrogen atoms of μ_4-TCNB. The six interligand N−Cu−N angles vary from 95.0(3)° to 119.4(3)°; see Table 2.

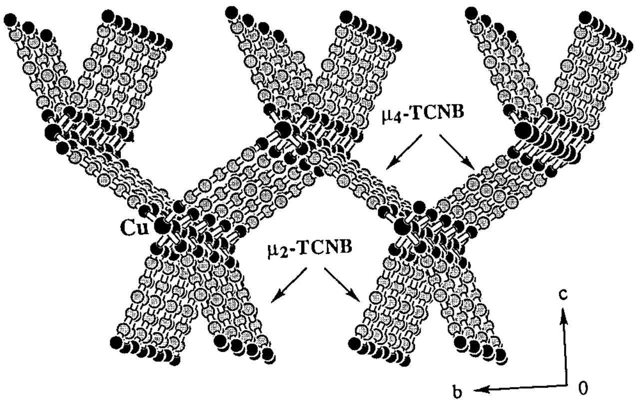

Figure 2. Packing view of [Cu_2(TCNB)$_3$]$^{2+}$ in **1** down the *a* axis.

It is shown in Figure 1 that the structure contains a Cu_4(μ_4-TCNB)$_4$(μ_2-TCNB)$_2$ core in which four copper atoms are bridged by four μ_4-TCNB groups forming a 30-membered ring. In addition, each μ_2-TCNB moiety bridges two metal ions within the ring to form a 14-membered ring. Such connections lead to a two-dimensional network of metal ions. Figure 2 gives a molecular packing view down the *a* axis. It can be seen that the pair of μ_4-TCNB and the pair of μ_2-TCNB ligands are associated around the tetrahedral metal center with N−Cu−N angles of 110.9(3)° and 95.0(3)°, respectively. They lie alternately above and below the *ab* plane through the Cu(I) ion. Thus, the polymeric cation [Cu_2(TCNB)$_3$]$^{2+}$ in **1** exhibits a unique topology with a zigzag sheet network. The solvated acetone molecules are incorporated in the network, and the PF_6^- anions are located adjacent to the μ_2-TCNB planar rings. The incorporated acetone molecules are not strongly bound in the lattice but are easily removed by drying the crystals in argon or air, resulting in the destruction of the crystal structure. This causes instability of the compound in the solid state. Neverthe-

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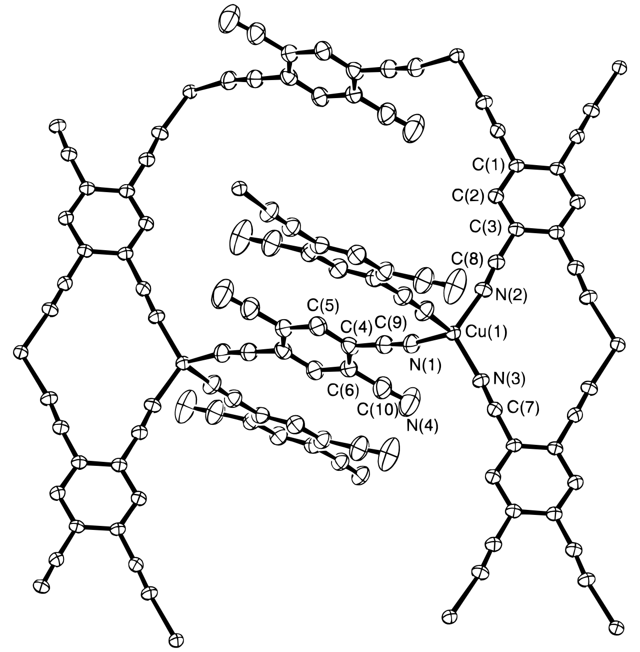

Figure 3. ORTEP drawing with atom-numbering scheme in **2** showing 40% probability level.

less, to the best of our knowledge, this is the first example of a copper(I) polymeric coordination compound of TCNB with two types of coordination, μ_4-TCNB and μ_4-TCNB.

Structure of $[Cu_2(TCNB)_3](PF_6)_2$ (2). It is interesting to find that a varied topological type of polymer **2**, despite having the same cation and anion as **1**, is obtained by using methylethyl ketone as the solvent instead of acetone. An ORTEP drawing of the asymmetric unit in **2** with atom-numbering scheme is shown in Figure 3. Complex **2** is composed of hexafluorophosphate anions and polymeric cations $[Cu_2(TCNB)_3]^{2+}$ without solvent molecules. Similar to **1**, there are also two types of the TCNB ligands involved. Each copper(I) ion is coordinated to four cyano-nitrogen atoms from two μ_2-TCNB and two μ_4-TCNB groups in a slightly distorted tetrahedral geometry, and the Cu−N bond distances vary from 1.943(5) to 1.983(5) Å (Table 2). However, the unique structural feature for **2** is that the bridging sites for the μ_2-TCNB ligands involve 1,4-cyano-nitrogen atoms instead of 1,2-cyano-nitrogen atoms as observed in **1**. Thus, a new self-assembly of a three-dimensional porous network appeared to be essentially caused by solvent, as described below.

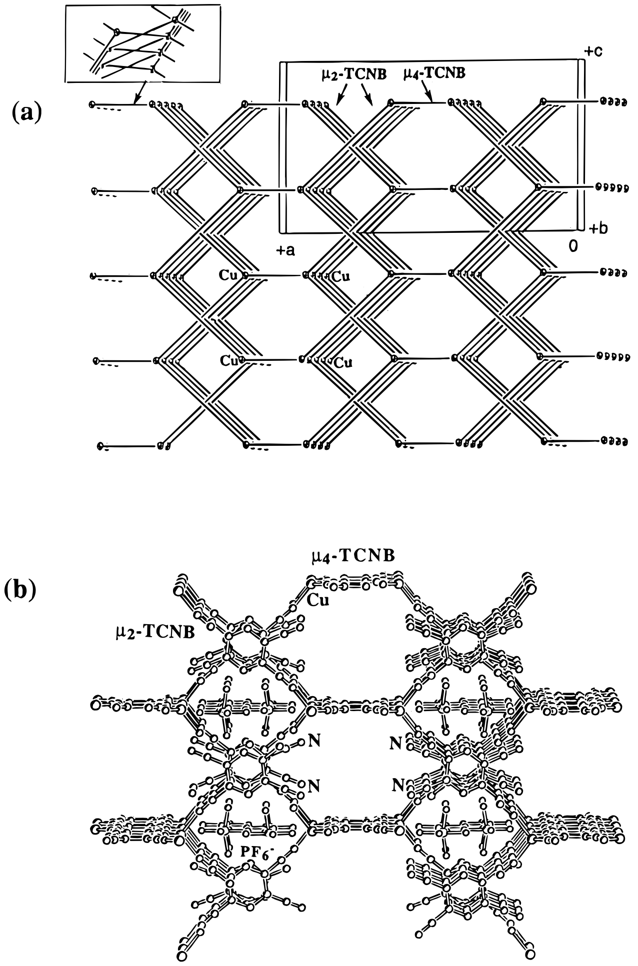

Figure 4. Interpenetration of two independent 3D network of $[Cu_2(TCNB)_3]^{2+}$ in **2**: (a) schematic view of interpenetrating; (b) 3D porous framework.

As shown by the crystal packing, Figure 4, the μ_4-TCNB and μ_2-TCNB molecules lie on two separate planes, which are completely orthogonal to each other. The N−Cu−N bond angle involving two μ_4-TCNB ligands around each metal center is 104.0(3)°, and that between the two μ_2-TCNB ligands is 118.0(2)°. There also exist 14-membered rings in **2**, but each ring is composed of two copper(I) ions bridged by two μ_4-TCNB ligands rather than by one μ_2-TCNB and one μ_4-TCNB molecule as found in **1**. Furthermore, the framework contains two other larger metal−ligand interconnected rings; one consists of four Cu(I) ions bridged alternately by two μ_2-TCNB and two μ_4-TCNB groups, Figure 3, and the second contains six metal ions linked alternately by four μ_2-TCNB and four μ_4-TCNB groups (visualized from Figure 4b). The extension of these interconnected rings along the *ab* and *ac* planes results in a three-dimensional framework. As can be seen from Figure 4, two such independent three-dimensional frameworks interpenetrate each other with the overlapping of μ_2-TCNB ligands along the *b* axis, between which the nearest nitrogen−nitrogen distance of 3.59 Å is slightly longer than the van der Waals interaction distance. The overall structure is made of such interpenetrated frameworks containing micropores of different size and varied functions. All uncoordinated cyano-nitrogen atoms are arranged in the bigger cavities (12.01 Å × 8.14 Å), and all hydrogen atoms (aromatic hydrogen) sit in the smaller cavities (8.43 Å × 6.42 Å), where the PF_6^- anions are incorporated as shown in Figure 4b. The PF_6^- anions are probably stabilized by the formation of hydrogen bonds between the aromatic hydrogen atoms and the fluorine ions, since the shortest F−H distance of 2.453 Å is within the hydrogen-bonding range of 2.17−2.54 Å.[35,36] These functional cavities may exhibit selective guest inclusion and provide potential use as a functional porous material.

Control of Crystal Structure by Solvent in Coordination Polymers. By changing solvents from acetone to methyletheyl ketone, with the same bridging ligand and metal salt, we successfully synthesized two types of copper(I) coordination polymers with two-dimensional zigzag sheet and three-dimensional porous frameworks, respectively. In both polymers, copper(I) ions have similar pseudotetrahedral environments and

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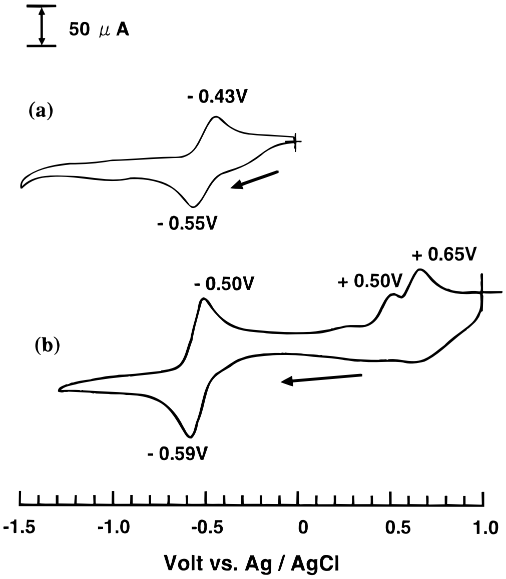

Figure 5. Cyclic voltammograms recorded in acetone at room temperature, 0.1 M tetrabutylammonium perchlorate, 100 mV/s scan rate: (a) TCNB; (b) complex **1**.

the four coordination sites are fully occupied by four bridging ligands, not by solvent molecules or counteranions. In addition, the two kinds of solvents have quite similar inductivities. Therefore, it is reasonable to suggest that the changing of crystal topologies of **1** and **2** is attributable to the steric factor of the solvents. Acetone, because of its smaller molecule, can readily attach to some specific positions of the complex network or be incorporated there, leading to an assembly of one type of configuration. On the other hand, for methyletheyl ketone, owing to its larger size, it is unfavorable to the selective interaction with the polymeric framework, resulting in the formation of another form of crystal structure. Generalization of the above findings in different metal−ligand−solvent systems is an ongoing topic of our studies.

Redox, Magnetic, and Conductive Behaviors. The results of a cyclic voltammogram of compound **1** together with free TCNB ligand are shown in Figure 5. Acetone was employed as the solvent because of the instability of **1** in other solvents. Solutions with an approximate 1 mM concentration were proved adequate for the cyclic voltammetric measurements at room temperature. On the basis of the established electrochemistry of TCNX (TCNX = TCNB, TCNP, TCNE, and TCNQ) molecules and their metal complexes,[5,8,37−39] complex **1** exhibits one quasireversible one-electron reduction and two irreversible one-electron oxidations at a reasonably slow scan rate of 100 mV/s; see Figure 5b. The reduction wave corresponds to that of TCNB itself, indicating the presence of $\mathrm{TCNB}^{\bullet-}$ in the complex. The reduction potential of −0.55 V is close to that of the noncoordinated TCNB (−0.49 V), implying an almost full compensation of the σ donor effect by the π back-bonding interaction; see Figure 5a.[4,5,11,40] Furthermore, the lower reduction potential of **1** compared to that of the free ligand suggests that the TCNB bridging ligand in **1** has an electron-acceptor property from metal ions.[38] The two oxidation waves, +0.50 and +0.65 V, which appeared in **1**, can be assumed to be a two-step oxidation of copper(I). The first oxidation (+0.5 V) is assigned as a normal Cu(I/II) couple, and the second oxidation is assigned as Cu(I/II) with the existence of Cu(II) in the neighboring coordination sites, since the oxidation potential is a function of the metal ion in the second coordination site.[41] Polymer **2** gives the same results as **1** in acetone solvent, which is in agreement with the results of NMR spectra, probably due to its easy turning into **1** when dissolved in acetone; see Figure 6.

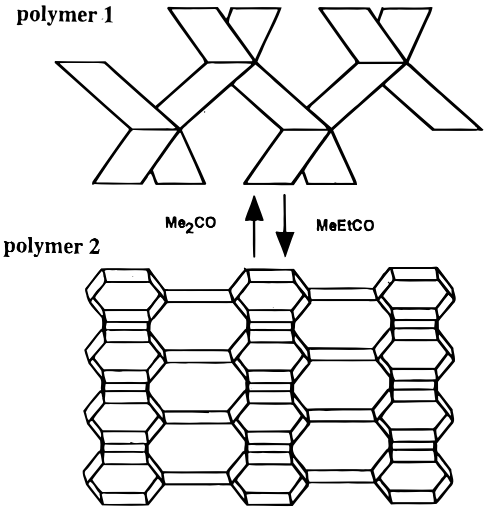

Figure 6. Schematic view of the structure exchange between **1** and **2**.

No ESR signal was observed for porous complex **2**, whereas **1**, with a zigzag sheet structure, exhibits an ESR signal at $g = 2.175$, indicating the existence of the Cu(II) ion[42] in **1** caused by the electron transfer from copper(I) to TCNB, which acts as electron acceptor for electron-rich metal.[5,8,43] This result is consistent with the redox interpretation. A very small amount of Cu(II) seems to be produced from the result of elemental analysis and ESR signal with low intensity. However, no ESR signal of $\mathrm{TCNB}^{\bullet-}$ was observed. This phenomenon, which happened in other TCNX complexes,[8,38,39,44] is probably due to the strong contribution from intermediate-spin metals to the LUMO[38] (fast relaxation[45]). The electrical conductivity of **1** with $\sigma_{25^\circ\mathrm{C}} = 2.21 \times 10^{-4}$ S cm^{-1} shows semiconducting behavior, while **2** is an insulator, indicating that **1** is more active than **2** in the electronic-transfer process.

Conclusions

By changing the solvent from acetone to methylethyl ketone, two novel and distinct polymeric coordination compounds of copper(I) with ligand TCNB, **1** and **2**, have been synthesized at room temperature. Though the two compounds have the same cation and anion, single-crystal X-ray analyses revealed that **1** exhibits a two-dimensional framework with a zigzag sheet arrangement between copper(I) ions, while **2** shows a three-

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dimensional porous network in which the cavities with different size and function group (or atom) are formed by the interpenetrating of two independent three-dimensional networks. PF_6^- anions are incorporated in the smaller cavities stabilized by hydrogen bonding. Polymer **1** exhibits an ESR signal of Cu(II) at $g = 2.175$ and displays a semiconducting behavior with $\sigma = 2.21 \times 10^{-4}$ S cm^{-1}. Polymer **2**, on the other hand, gives no ESR signal, and it is an insulator. When the two compounds are dissolved in the acetone solvent, they give the same redox behavior in cyclic voltammogram and NMR spectra, probably due to the interconversion of **2** and **1** in solution.

Acknowledgment. This work was partially supported by a Grant in Aid for Science Research [Nos. 09554041, 10440201, and 10016743 (priority areas)] from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page

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